Toxicity Identification Evaluation (TIE) for Sediments

NAVFAC
(Naval Facilities Engineering Command)

NAVFAC

Presentation Overview

- Overview of TIEs
  - TIE Basics
  - Potential Value Added to Ecological Risk Assessments
- Questions and Answers When Considering the Initiation of a TIE
  - Benefits and Limitations
  - Costs
  - Timing a TIE Study
  - Assessing Your Site
  - Logistical Considerations
- NAVFAC TIE Project
  - Initiation
  - Case Studies
- Summary and Conclusions

Problem Statement and Solution

Problem Statement:

- Overly conservative or inappropriate cleanup levels can increase the cost of remediation of contaminated sediments

  Current Practice:

  - Site cleanup levels may not be developed for COCs directly responsible for toxicity,
  - Does not always take into account site-specific information,
  - Does not rule out confounding factors as contributing to toxicity

Solution:

- Use TIE process to help determine chemical-specific cleanup levels and any toxicity due to confounding factors

Note: For more information on confounding factors, see May 1999 Contaminated Sediments RITS presentation

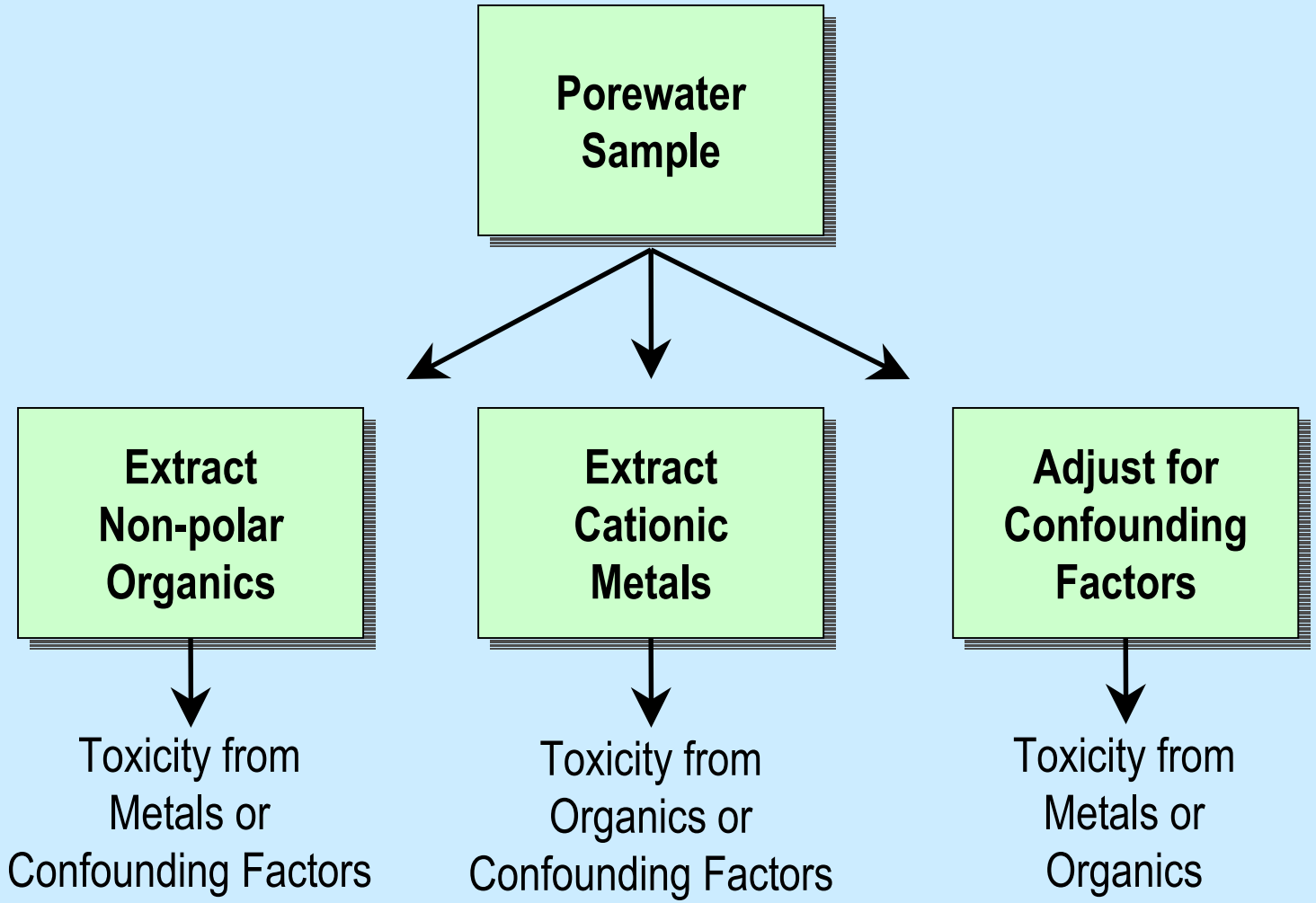
TIE Technology Description

- A Toxicity Identification Evaluation (TIE) is a series of lab tests that manipulate physical/chemical properties of sediment porewater to bind classes of chemicals and certain confounding factors, thus rendering them biologically unavailable

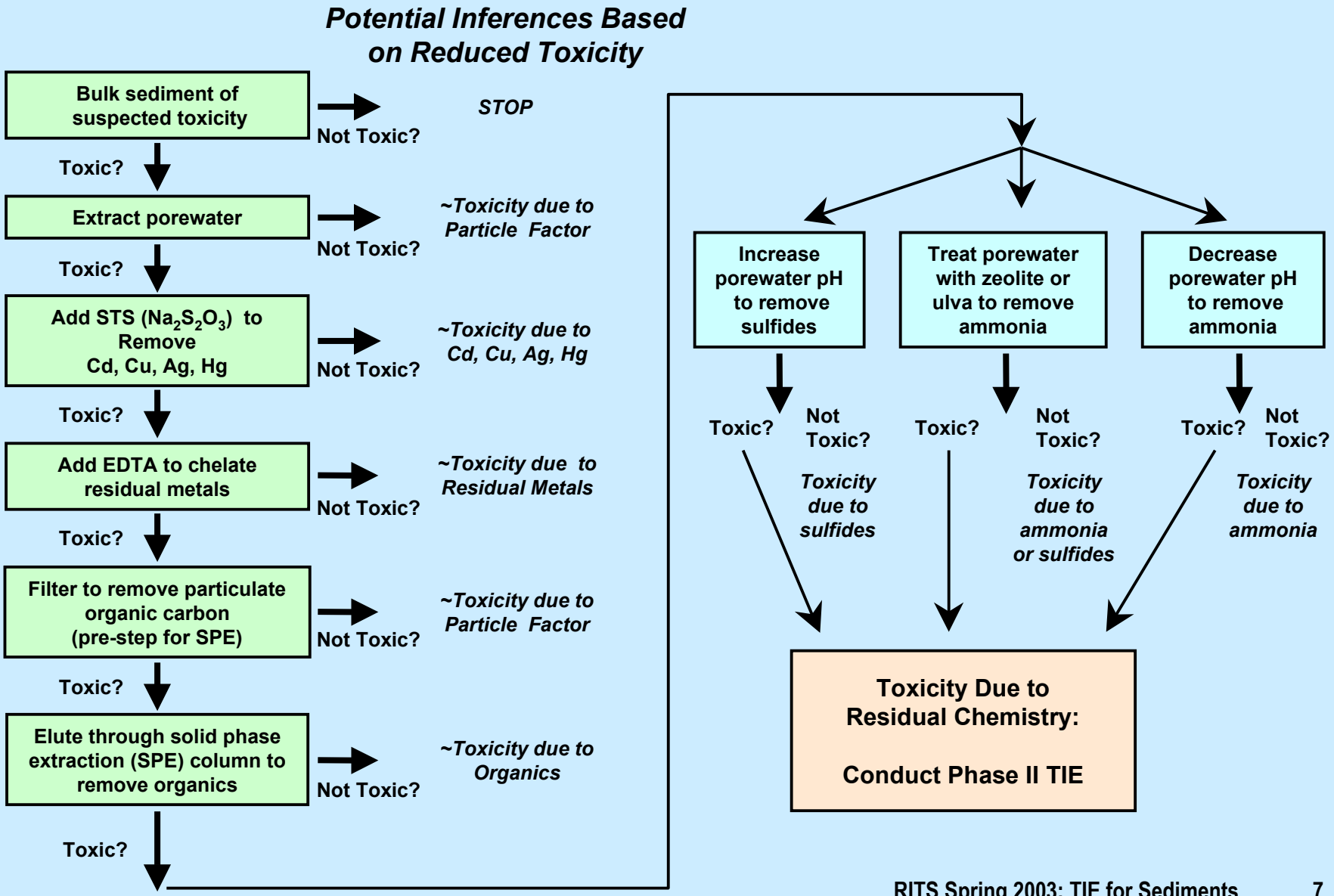
TIE History

- Initial TIE procedures developed by U.S. EPA to assist in understanding causes of toxicity associated with effluent sampling
- U.S. EPA modified procedures to apply to sediment porewater (U.S. EPA, 1991, and U.S. EPA 1996)
- Modification of these procedures has occurred
  - Taken from laboratory applications to field applications
  - From parallel to sequential extraction (NAVFAC TIE Project)
  - Adapted for application using bulk sediment instead of sediment porewater (see Ho et. al., 2002 for more information)

U.S. EPA TIE Procedure (Parallel Approach)



Flow Diagram for Sequential TIE: Fractionation, Testing, and Interpretation



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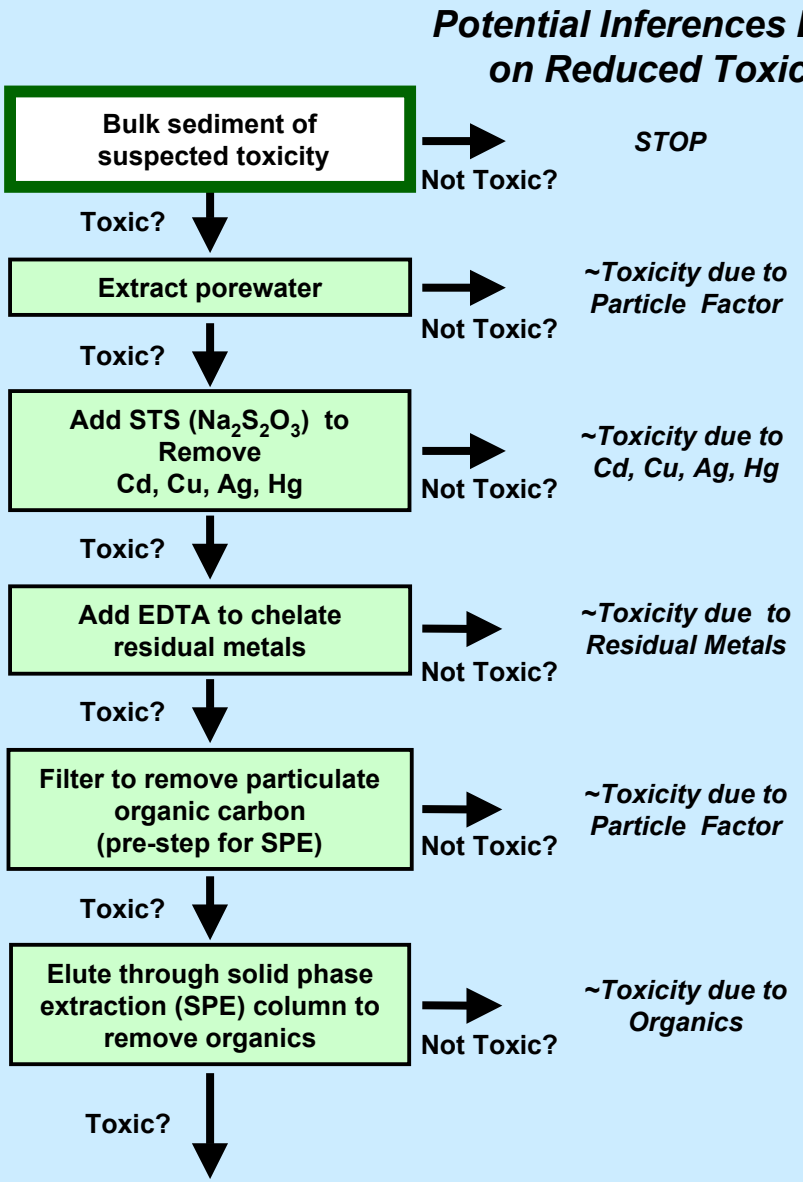

- Bulk sediment tested according to uniform sediment toxicity testing procedures to confirm toxicity
- **No toxicity** indicates that the **TIE should stop**
- **Toxicity** indicates that the **TIE may be continued** to discover the source of toxicity

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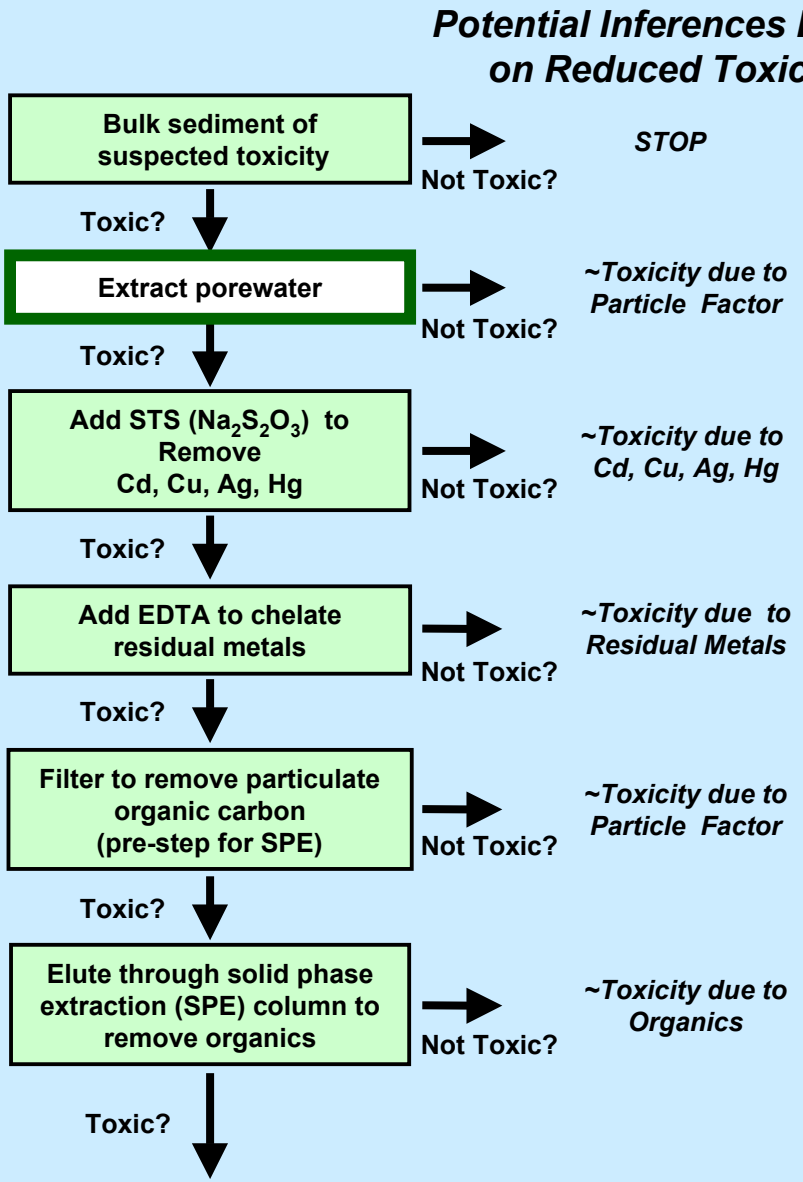
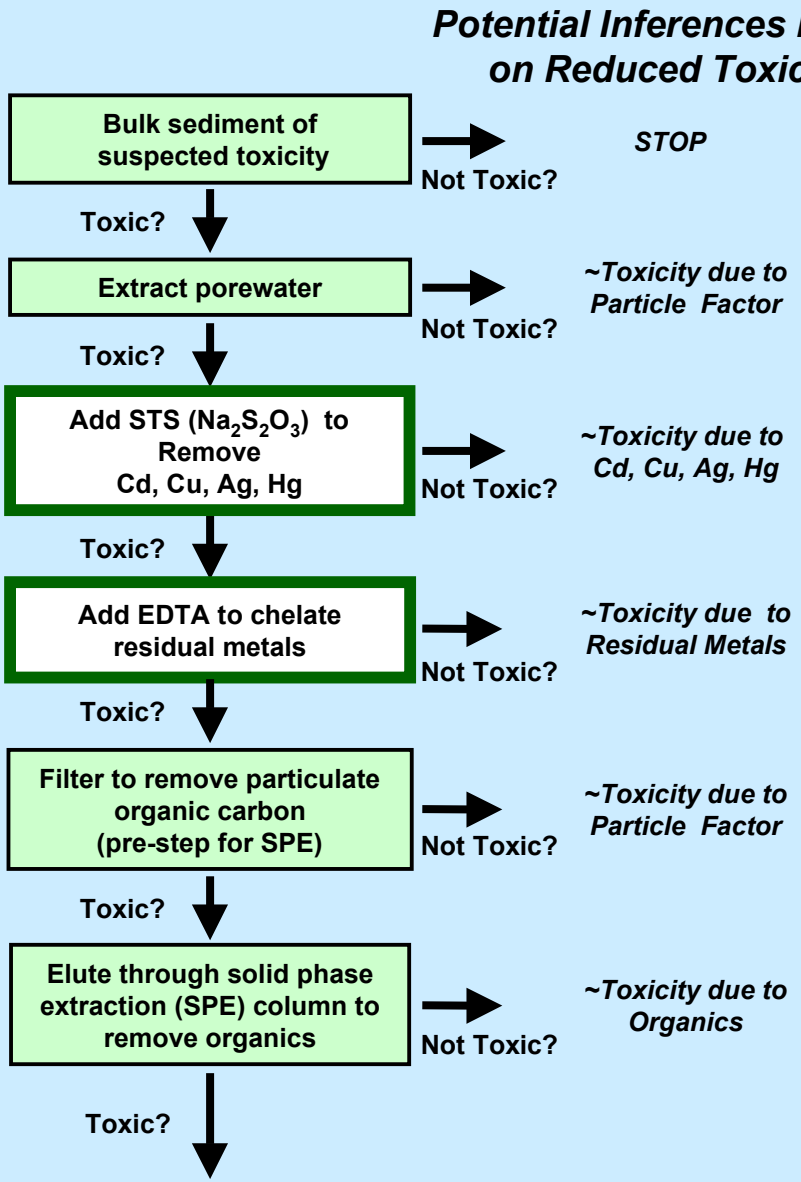


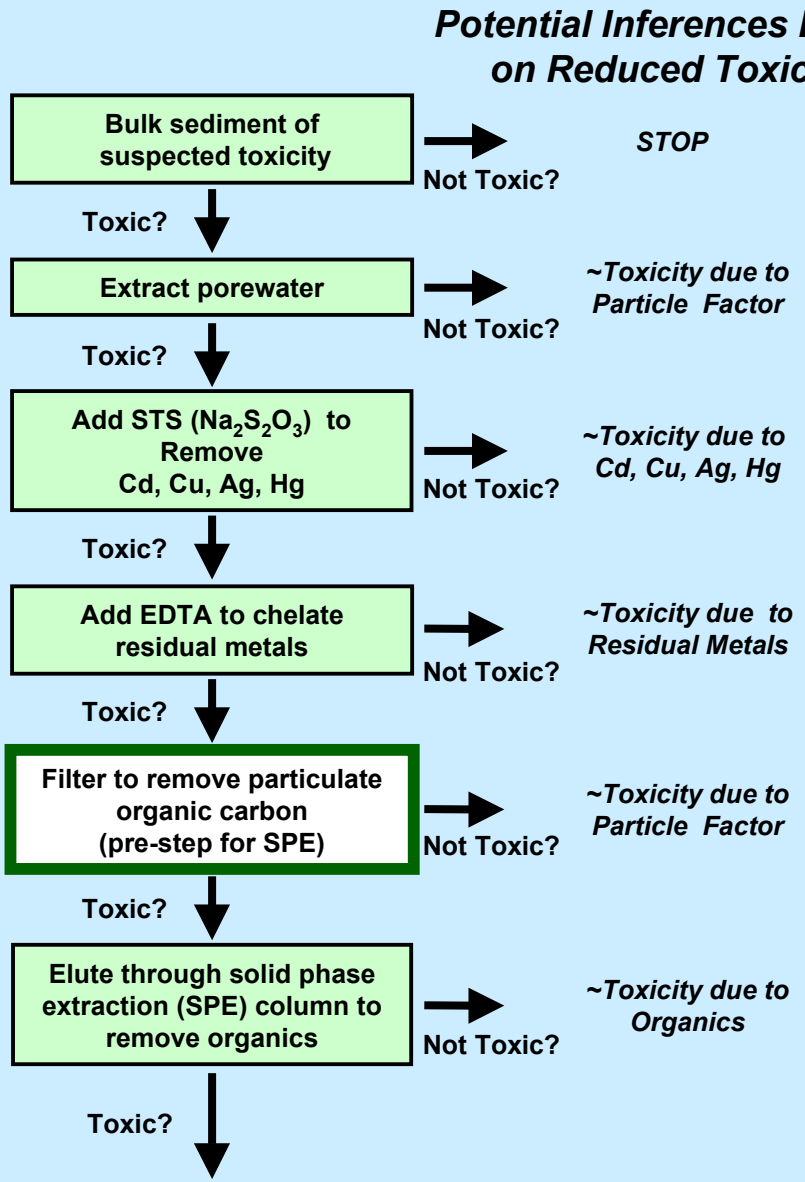
- Porewater extracted from the bulk sediment undergoes toxicity testing. This provides a baseline for comparison of treated samples.
- **No toxicity/reduced toxicity** indicates that the toxicity was in some way associated with the **particles of sediment**
- **Toxicity** indicates that the **TIE may be continued** to discover the source of toxicity

Flow Diagram for Sequential TIE: Fractionation, Testing, and Interpretation



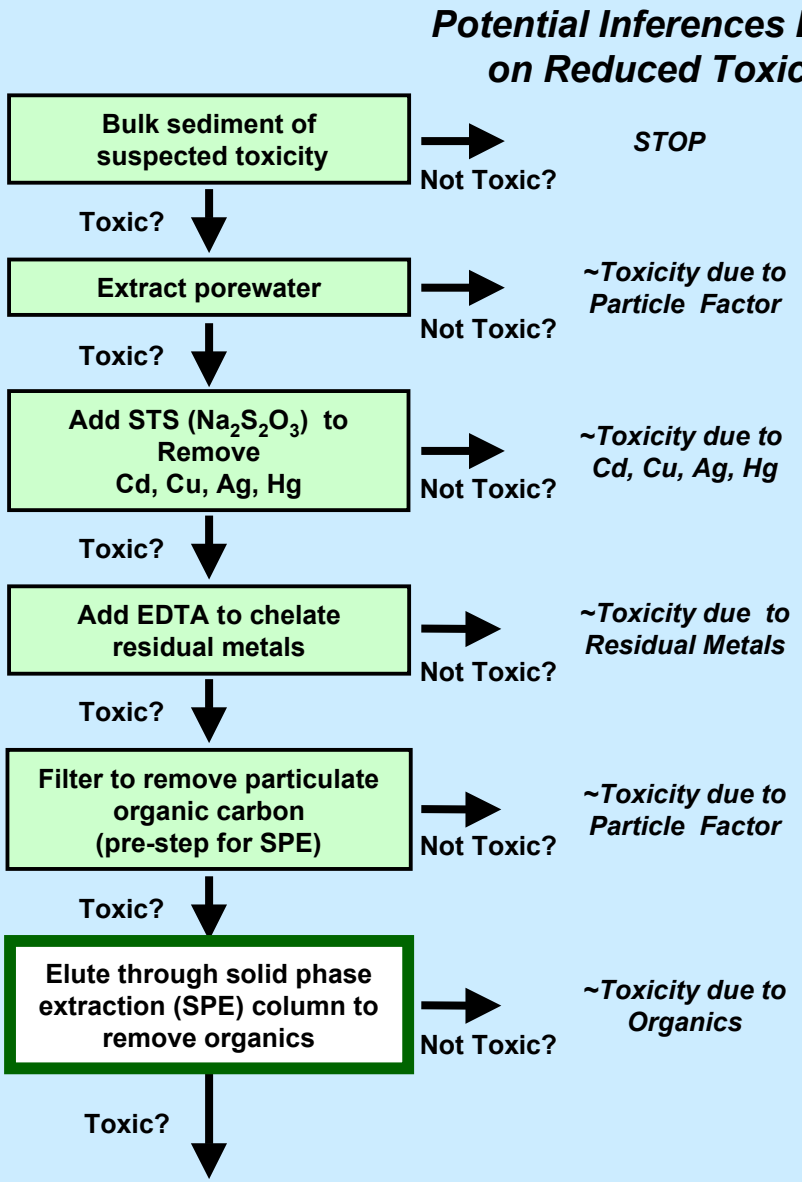
- Porewater is treated with STS to remove toxicity associated with a subset of cationic metals
- Porewater is next treated with EDTA to remove toxicity associated with divalent cationic metals
- **No toxicity/reduced toxicity** indicates that the toxicity was associated with **metals**
- **Toxicity** indicates that the **TIE may be continued** to discover the source of toxicity

Flow Diagram for Sequential TIE: Fractionation, Testing, and Interpretation



- Porewater is filtered to remove suspended particles that could cause toxicity or clog the SPE filter
- **No toxicity/reduced toxicity** indicates that the toxicity was associated with **suspended particles**
- **Toxicity** indicates that the **TIE may be continued** to discover the source of toxicity

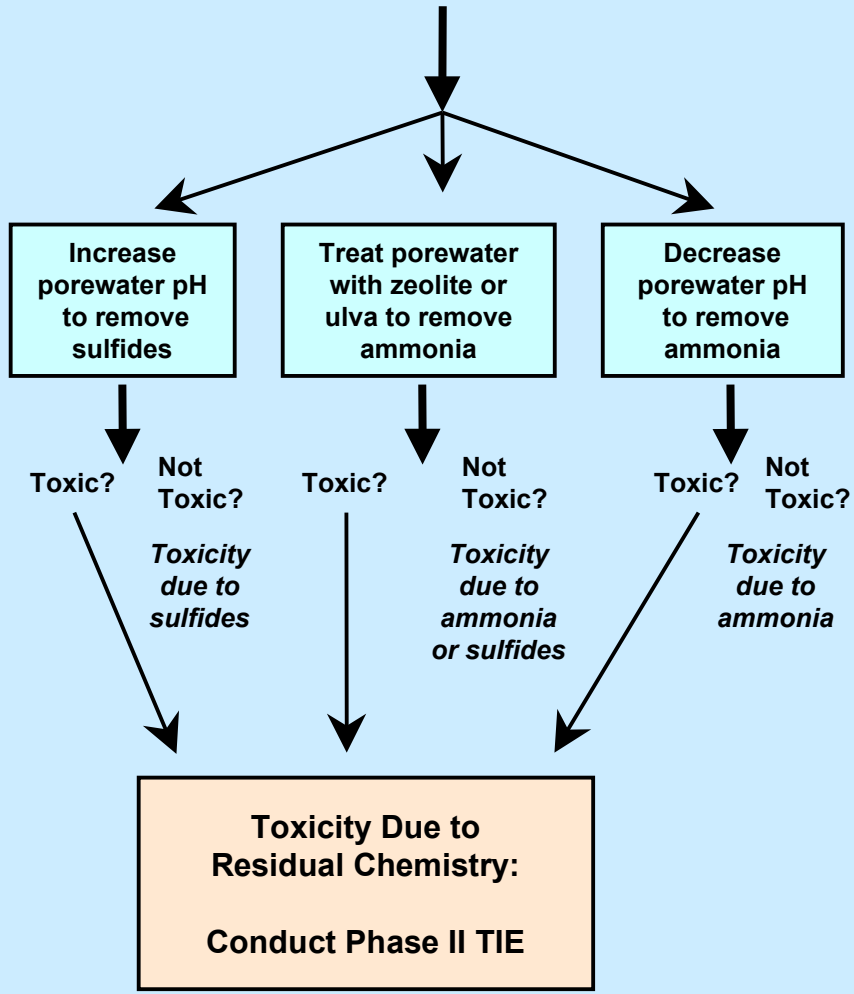
Flow Diagram for Sequential TIE: Fractionation, Testing, and Interpretation



- Filtered porewater is eluted through a Solid Phase Extraction (SPE) column to remove organic compounds
- **No toxicity/reduced toxicity** indicates that the toxicity was associated with **organics**
- **Toxicity** indicates that the **TIE may be continued** to discover the source of toxicity

Flow Diagram for Sequential TIE: Fractionation, Testing, and Interpretation

- The treatments for confounding factors occur in parallel
- Porewater is treated with zeolite (freshwater) or ulva (saltwater) to remove ammonia
- **No toxicity/reduced toxicity** indicates that the toxicity was associated with **ammonia**
- Porewater pH is manipulated to determine toxicity due to sulfides and ammonia
- **No toxicity/reduced toxicity with increased pH** indicates that the toxicity was associated with **sulfides**
- **No toxicity/reduced toxicity with decreased pH** indicates that the toxicity was associated with **ammonia**



Potential Benefits of TIE Study

Remedial Investigation of Sediment Site

- During Baseline Ecological Risk Assessment (BERA) evidence of sediment-based toxicity can be found and can not be easily attributed to any specific contaminant (e.g., mixture of chemicals)
  - TIE Study can assist in resolving cause-and-effect relationships as they relate to the observed sediment toxicity
- Developing PRGs during RI/FS
  - Utilizing all data, "Limiting COCs/Risk Drivers" can be identified

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Technology Benefits

- Assists in understanding cause and effect relationships as they relate to sediment toxicity
- Coupled with chemistry, can assist in identifying the "Limiting COCs/Risk Drivers" for a sediment site
- Can assist in identifying whether site-related COCs and/or confounding factors are contributing to observed toxicity
  - Better understanding of toxicity can lead to better risk management decisions
  - Results can potentially lead to overall cost reduction for remediation

Technology Limitations

- As with all technologies, TIEs cannot promise certainty
  - Results might show mixture of chemicals are causing toxicity
  - Not all causes of toxicity may be resolved (not possible for all chemicals)
- Costs of TIE Study can be expensive and must be balanced with potential remediation costs
- Does not address concerns that can arise from bioaccumulative chemicals (e.g., PCBs)
- Does not address chronic toxicity

What are the Costs of TIE Study?

Activity	Low End Costs; single inexpensive toxicity test (no fieldwork or chemistry)	High End Costs (with fieldwork and chemistry)
Study Design and Work Plan Preparation	$500	$1,300
Field Sampling	None – covered by other site studies	$2,500
TIE Preparation and Testing		
Bulk Sediment Testing	None – covered by other site studies	$750 - $1000
Porewater Extraction	$100 syringe	$200 (high speed centrifugation)
TIE Manipulations	$1,000	$1,000
ToxicityTesting	$200	$2,000
Chemical Analyses		
Bulk Sediment (e.g., metals, organics, TOC, SEM, AVS)	None – covered by other site studies	$1,500
Porewater Metals	$130	$130
Data Presentation		
Synthesis and Analysis	$400	$1,200
Report Preparation	$400	$1,200
Per Sample Total Costs	$2,750 (1 sed.)	$12,030
Total Costs[1]	$2,750 (1 sed.)	$164,450[2]

[1]Assume 15 samples for all but TIE preparation and testing, where 10 samples are asssumed.
[2]Where field activities and chemistry costs are not incurred, high-end cost estimate would be $104,450.

How do You Evaluate a Sediment Site for Completing a TIE Study?

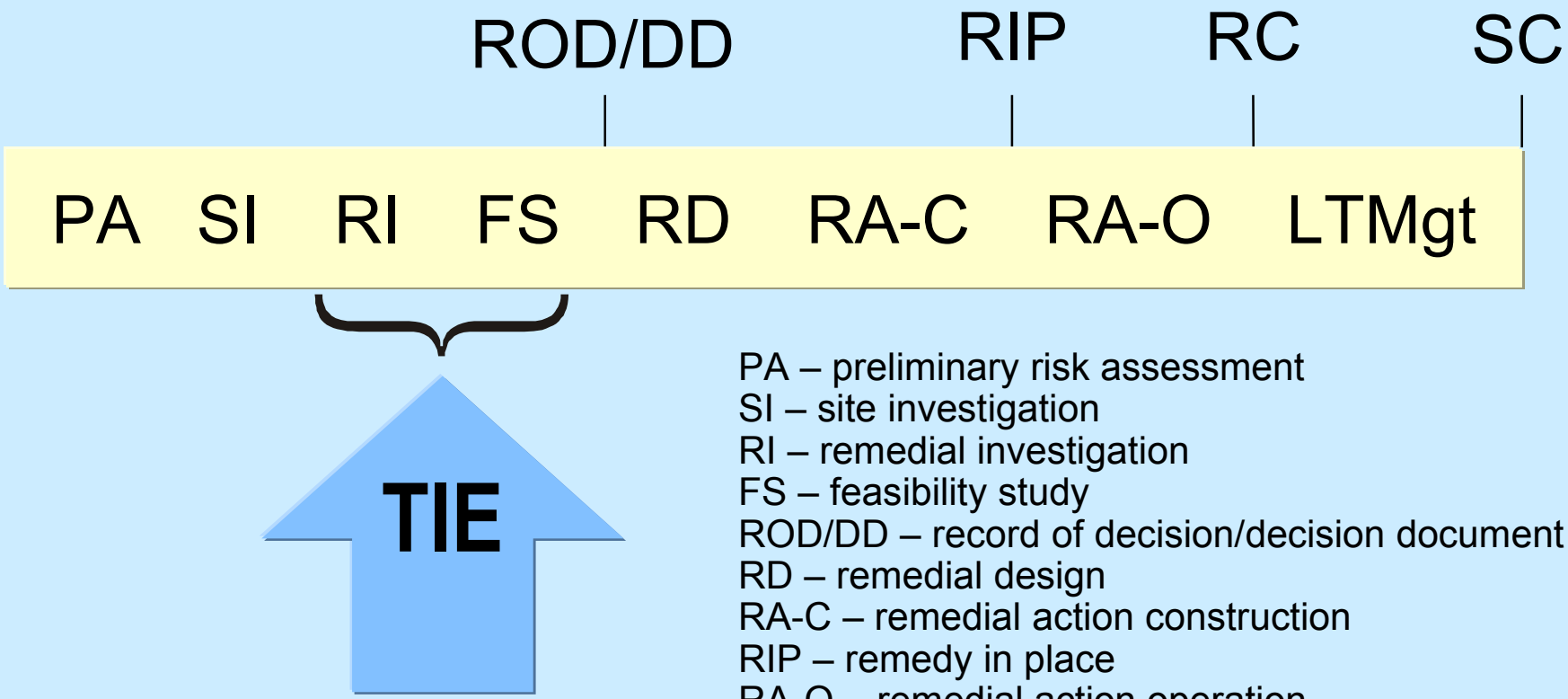
- A TIE Study is **NOT** for all sediment sites
- TIEs are broadly applicable to a wide variety of sediment sites and data types, particularly where actionable risk is identified for acute effects on aquatic organisms.
- Balancing of costs and needs has to be evaluated

How do You Evaluate a Sediment Site for Completing a TIE Study? (cont.)

- If bioaccumulation up the food chain is believed to drive risk at a site, resolving causes of toxicity may not affect risk management decisions
- An evaluation of previous data needs to be completed
- Regulators and/or Biological Technical Assistance Group (BTAG) members should be receptive to accepting and including results of TIE Study in risk management decisions

When Should a TIE Study be Considered?

- TIEs are generally most useful after completion of a preliminary risk assessment, and preferably before the FS is completed



- Allow 6 to 8 months to plan a TIE study

PA – preliminary risk assessment
SI – site investigation
RI – remedial investigation
FS – feasibility study
ROD/DD – record of decision/decision document
RD – remedial design
RA-C – remedial action construction
RIP – remedy in place
RA-O – remedial action operation
RC – response complete
LTMgt – long-term management
SC – site closeout

When Should a TIE Study be Considered? (cont.)

- Toxicity should have already been observed in previous studies
- Previous information indicates toxicity may likely occur during collection of BERA information
  - For example, numerous chemicals exceed benchmarks that indicate probable effects/toxicity
    - Recently, included in approach for BERA at PNBC Reserve Basin
- However, if uncertainty regarding the source(s) of toxicity remains during the FS, then a TIE may serve as a "better late than never" option (e.g., FS Validation Study)
- While each TIE study is unique, as a general rule six to eight months should be allowed for the completion of a sediment porewater TIE, from planning to final reporting

What are the Logistical Considerations?

- Many logistical considerations are similar to those of other types of sediment investigations
  - Time of year
  - Sampling equipment needed (e.g., Do you need a boat to collect samples?)
  - Availability of test organisms
  - Station positioning
- Biggest consideration is if TIE Study will be completed alone or in conjunction with other studies/sampling
  - Economy of scale

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Case Study 1
Goss Cove, CT (Prior to TIE Project)

- Formerly a portion of the Thames River, isolated by construction of railroad bed
- Northern portion of cove used as landfill between 1946-1957
- Remaining cove sediments low in oxygen
- Chemicals in cove sediment (PCBs, metals, pesticides) at levels of potential concern
- Preliminary investigation found toxicity and concluded risks to aquatic biota did exist

TIE Used to Investigate Toxicity

- TIE showed that toxicity is due to ammonia (confounding factor) and not site-related COCs
- No Further Action Finding proposed and accepted by regulators
- Avoided Navy costs of $2M in potential sediment remediation

NAVFAC TIE Project

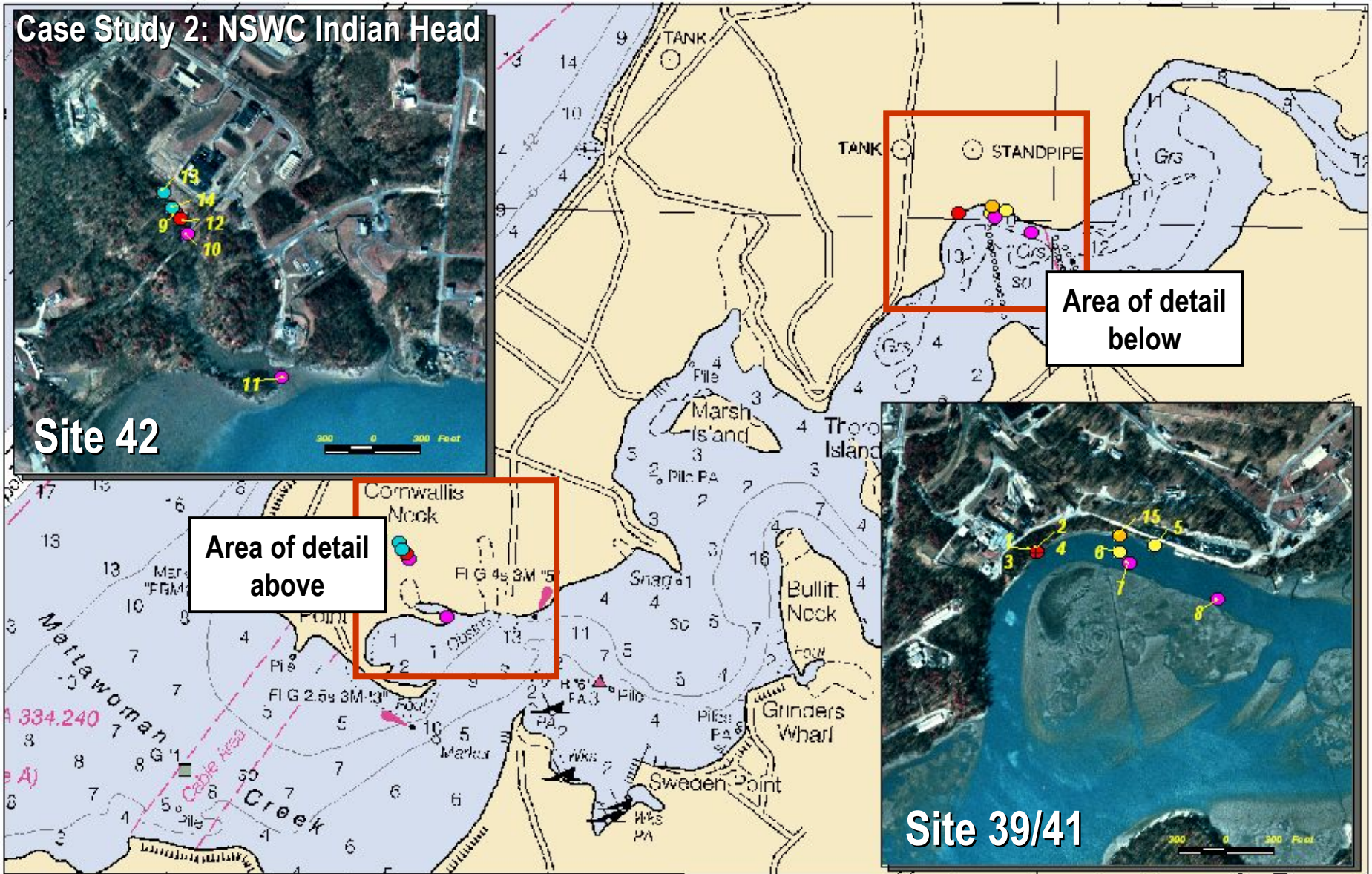
- TIE Project was funded through the Navy's Pollution Abatement Ashore Technology Demonstration/Validation Program Project YO817
  - Alternative Restoration Technology Team (ARTT)
- Project included:
  - Demonstration/Evaluation of Sequential TIE approach at two locations
    - Different water body types
    - In different U.S. EPA Regions
  - Evaluation of alternative extraction techniques
  - Development of User's Guide and White Paper

Selecting Sites for TIE Project

Site Selection Criteria	NSWC Indian Head, MD	Hunters Point Shipyard, CA
Acutely toxic sediments?		
COCs above screening benchmarks?		
Type of aquatic environment	Fresh to tidal fresh	Marine
U.S. EPA Region	3	9
NAVFAC Component	EFA Chesapeake	EFD Southwest
Types of contaminants	Silver; other cationic metals; ordnance; organics	Cationic metals; organics
Confounding factor identified	Ammonia	Ammonia

Case Study 2
NSWC Indian Head

- 15 sediment samples were collected and tested for bulk sediment toxicity
  - 6 samples from unnamed stream adjacent to Site 42 (Olsen Landfill)
  - 8 samples in Mattawoman Creek offshore of Sites 39/41 (organics plant and scrap yard)
  - 1 sample taken adjacent to Site 28 – Original Burning Ground in Mattawoman Creek upstream of Sites 39/41
- Porewaters from 10 toxic bulk sediment samples were tested in a sequence of TIE experiments



STATIONS SELECTED FOR INDIAN HEAD TIE DEMONSTRATION

2000 0 2000 4000 Feet

Legend

- High TPH or Nitrocellulose
- High Mixed Metals
- High Ag
- High Ag (Replicate)
- Total NH3 correlates with Toxicity

An Employee-Owned Company

B.D. Andrews, SAIC, 9 AUG 00

File: Indian_hd_39_41

B.D. Andrews, SAIC, 9 OCT 00

Lower Site 42 Environment

Confluences of the unnamed stream and Mattawoman Creek downstream of Site 42 – Olsen Road Landfill

Site 39/41 and Site 28 Environments

Sites 39/41 along the Mattawoman Creek shoreline.

Shoreline of Mattawoman Creek looking towards Site 28.

NSWC Indian Head TIE Summary

Site 42 results:

- In unnamed stream, the TIE demonstrated that porewater toxicity was not due to silver, which was previously identified as the target COC for the stream (based on Site 42 RI findings)
- Ruled out PAHs and PCBs as causes of toxicity in unnamed stream
- Sample filtration resulted in partial toxicity removal at two stations, suggesting toxicity was associated with the particulate fraction of the sample and not COCs

NSWC Indian Head TIE Summary (cont.)

Site 39/41 and results:

- Ruled out PAHs and PCBs as causes of toxicity in Mattawoman Creek
- Ammonia was identified as a principal source of toxicity in one Mattawoman Creek sample, and was shown to contribute to toxicity in several other samples
- The TIE treatment failed to fully remove toxicity in one porewater sample

Site 28 results:

- TIE results and chemical analyses indicated that zinc was the principal COC from the sole burn pit sediment sample

Summary of TIE Findings

Site	Sample	*Hyalella* Toxicity Rating		Suggested Toxicity Source in Sediment
		Bulk Sediment	Porewater TIE	
39/41	IH-02	+	+++	Ag, b-BHC, NitroB, geotech.
	IH-06	+	++	b-BHC, Mn, NH_4
	IH-08	++	++	NH_4
	IH-15	+++	+++	Zinc
42	IH-11	+++	++	SED, Mn
	IH-13	++	+	SED

Toxicity rating from low (+) to high (+++)

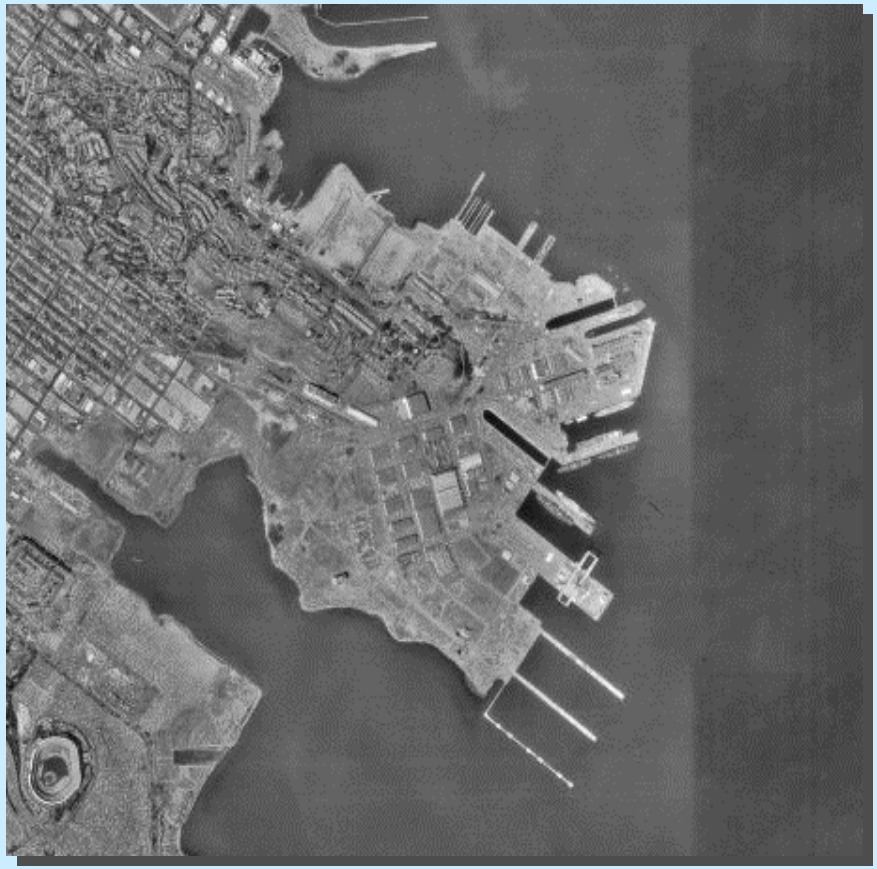
SED = toxicity due to particulate fraction or longer duration of sediment exposures

Case Study Summary – Validation of Project Objectives

- TIE provided clarification of COCs in unnamed stream for proceeding with the Site 42 FS and ROD
- Provided input for formulating the greater Mattawoman Creek study completed by EFA Chesapeake
- Work Plan and TIE Summary Report were accepted by regulators with very few comments

Case Study 3
Former Hunters Point Naval Shipyard, CA – Parcel F

- TIE demonstration integrated as part of Hunters Point Validation Study completed by SWDIV
- SWDIV shared split bulk sediment samples, as well as stock of sea urchins
- Information collected as part of validation study was used to correlate the results of the TIE

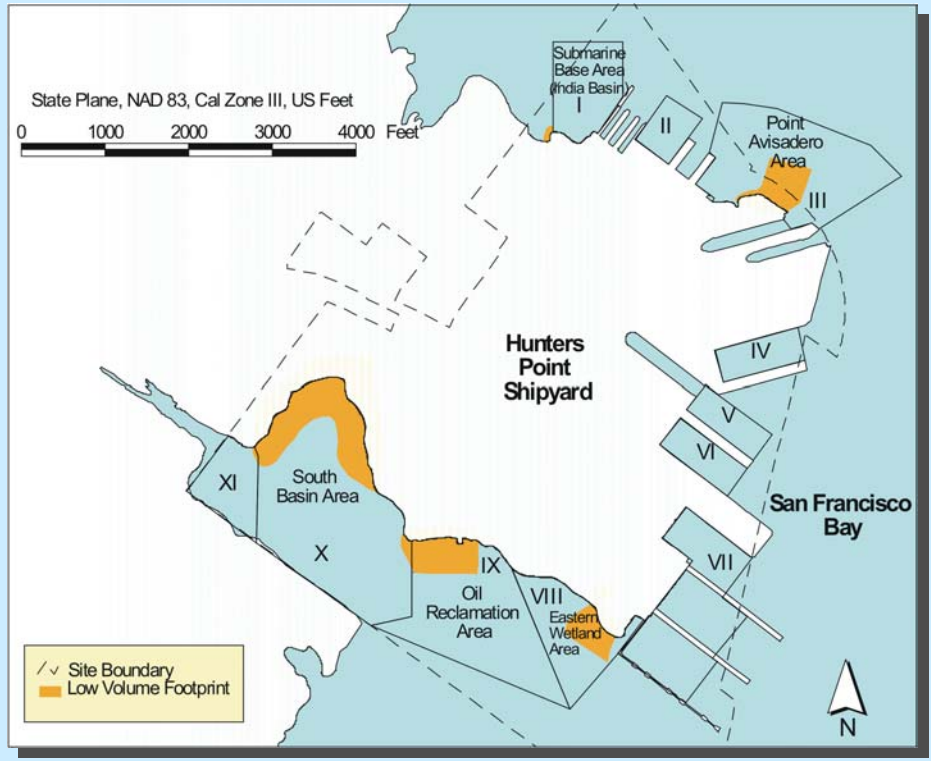


Why was TIE Initiated?

- Previous toxicity testing completed in Parcel F showed toxicity
- Evaluation of previously observed toxicity completed
  - Results suggested that observed toxicity was due to ammonia concentrations (i.e., confounding factor)
- TIE study initiated to provide information on chemical causality for toxicity that might be observed during testing planned for the Validation Study

TIE Stations at Hunters Point

- TIE run on porewaters collected from sediments collected from 8 stations located in 4 areas of Parcel F
  - Zone III (Point Avisadero Area)
    - 2 sediment samples from 1 station at different depths
  - Zone VI (Eastern Wetland Area)
    - 1 sediment sample
  - Zone IX (Oil Reclamation Area)
    - 1 sediment sample
  - Zone X (South Basin Area)
    - 5 sediment samples, 1 at two depths
- TIE also run on reference location sediments used for Validation Study



Results of TIE Study

- Ammonia was the predominant source of toxicity removed by TIE procedures, but other contributors to effects were observed with one test species (purple urchin)
  - Some toxicity reductions due to STS reduction and EDTA chelation were observed and correlated with elevated porewater concentrations of metals (Al, Cu, Mn, and Zinc)
    - A similar correlation was also observed at the reference station, indicating that metals-related toxicity may not be site-specific
- Toxicity did not differ substantially with depth in the two stations where surface and subsurface sediments were represented

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Summary

- Three important things to remember about TIE Studies for Sediment Sites
  - TIE Studies can assist in making better risk management decisions for a sediment site by helping to identify causes of observed toxicity and "Limiting COCs/Risk Drivers"
  - Cost savings can be realized, but must be balanced with the costs of completing an actual TIE Study
  - Before pursuing the completion of a TIE Study an evaluation of previous data and of potential remediation costs for a sediment site need to be completed

Conclusions

- TIEs are another investigative tool that can be utilized in assessing ecological risks at sediment sites
- A thorough evaluation should be completed prior to completing a TIE Study to identify if its use could provide valuable input for risk management decisions
- As with other technologies, the technology is only as good as the performer
  - A contractor experienced in completing and interpreting results of sediment-related toxicity testing should be used to design and implement a scientifically sound TIE Study

Finding More Information

- U.S. EPA Publications
- Literature
- NAVFAC TIE Project produced two deliverables to help assist in what a TIE is, how to evaluate a site, and how to actually complete a TIE study
  - White Paper
    - Provide brief overview
  - Guide for planning and conducting sediment porewater TIEs to determine causes of acute toxicity at Navy Aquatic Sites
    - Provide more detailed information
  - Both documents can be found on NFESC and NAVFAC ERA web sites
    - NFESC web site - http://enviro.nfesc.navy.mil/erb/
    - NAVFAC ERA web site - http://web.ead.anl.gov/ecorisk/

References

Documents

- U.S. EPA. 1991. Methods for aquatic toxicity identification evaluations: Phase I toxicity characterization procedures. 2nd ed. EPA/600/6-91-003. Environmental Research Laboratory, Duluth, MN.
- U.S. EPA. 1996. Marine Toxicity Identification Evaluation (TIE), Phase I Guidance Document. EPA/600/R-096/054. U.S. EPA Office of Research and Development, Washington, DC.
- Ho, K.T., R. Burgess, M.C. Pelletier, J.R. Serbst, SA. Ryba, M.G. Cantwell, A. Kuhn, P. Raczelowski. 2002. An overview of toxicant identification in sediments and dredged materials. *Mar. Poll. Bull*. 44: 286-293.

Web Sites

- http://enviro.nfesc.navy.mil/erb/
- http://web.ead.anl.gov/ecorisk//

NAVFAC Points of Contact

NFESC

- (805) 982-4798
- (805) 982-4890

EFANE

- (610) 595-0567 x188
- (610) 595-0567 x183